Evaluation of absorption capacity of nanoparticles and non nanoparticles of ZnO as solid agents able to eliminate H_2S

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1. BACKGROUND

Before using natural gas as fuel, it has to be conditioned through different processes. During these processes it is required that different contaminants be eliminated due to the fact that they can affect fundamental aspects such as: decrease in calorific power, human health and ecosystem effects besides damage on infrastructure during the whole natural gas value chain. Hydrogen sulphide (H_2S) is one of these contaminants due to its undesirable corrosive and poisonous effects. Removal of H_2S from natural gas can be done by different technologies commonly in used today. Sweetening process is a general term used for eliminating acid gases as H_2S.

Natural gas sweetening has become more relevant in Venezuela since new projects in natural gas area foresee an increase in the production from $6{,}300\times10^6$SCFD to $11{,}500\times10^6$SCFD in 2012. All these new developments require H_2S to be eliminated. Furthermore, to achieve the quality specifications required in national legislation of natural gas impose to work on this area. New changes on law projected for the next six years will be more severe respect to current specifications.

One kind of technology used for sweetening involves interaction between the natural gas and a solid capable of reacting and/or adsorb contaminants, specially H_2S. Inside the reactor, the process scheme of these technologies allows this contaminant to be absorbed or adsorbed and its presence decreases in the gas stream. When the solid is finally saturated, the reactor is emptied and refilled in the case of non regenerative solid agent or regenerated when is possible.

PDVSA Intevep has been researching on H_2S removal in natural gas streams using receptors with based on metallic oxides such as iron oxides and zinc oxide.

Some industries are producing this type of oxides at nano scales in order to take advantage of the increase in surface area. A comparison between both cases (at nano and non nano scale) is a contribution in this study to find out whether it is necessary to work at nano scale. This type of study, is aimed to produce a competitive product able to decrease or eliminate the amount of H_2S. As a part of these studies, this work is focused on laboratory tests which helped to make a comparison between nano and non nanopowder of ZnO besides the study of the water effect on these conditions.

2. AIMS

In this study a comparison between two types of ZnO (at nano and non nano scale) is made as a contribution to find out advantages of working at nano scale, including studies on the effect of water during the chemical interactions between ZnO and H_2S according equation 1.

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad (1)$$

3. METHODS

Experimental studies for this work include: physical characterisation, absorption capacity test and phases identification (before and after the absorption tests).

3.1. Physical characterisation of samples

Two types of ZnO were studied; nanoparticles and non nanoparticles. The main physical features considered in this project are:

- **Specific surface area:** Using equipment that works by physical adsorption with nitrogen. This parameter is very important for the information connected to the exposure during the chemical reactions.
- **Pore volume and average pore diameter:** Represents the whole void space in the solid particle and mean diameter of the porous respectively. By these pathways the gas can diffuse through the solid. Then the gas can interact with the solid phase on the external surface and in the internal porous surface.
- **Bulk and particle density.** Terms usually used in powder system; the first refers to the total system density which considers the whole volume including the voids, meanwhile the latter does not take into account the opening spaces volume. With both densities the porosity can be calculated with equation 2.

$$Porosity = 1 - \frac{D_{BULK}}{D_{PARTICLE}} \qquad (2)$$

3.2. Phases identification before the chemical reactions

Nanoparticles and non nanoparticles of ZnO were tested by the X-ray diffraction technique. This is a non destructive test that helps to know which types of phases can occur in a crystalline system. The principle is based on how the X-ray can path through and be reflected in a solid. It regards the lattice parameter of the unit cells that can be presented. The range of wavelength corresponds to the X-ray (0.5-50 Å) and the atomic dimension of the lattice parameter are the condition that allows the diffraction phenomenon to appear and represented by equation 3.

$$2dSen\theta = n\lambda \qquad (3)$$

This is the Bragg's Law and the variables involved are;

d: distances between two parallel planes in the crystal lattice
θ: angle between incident rays and scattering planes
λ: wavelength of X-ray
n: integer number which refers to the order of reflections

Before chemical reactions the reactant purity is also quantified in order to support the phase identification in this stage.

3.3. Absorption capacity test

3.4.1. General principle

This stage is the core of the experimental part of this study. These tests are carried out in static conditions. It means that a gas solution is introduced into a reactor, and a physical-chemical phenomenon is expected to occur. The reactor (50 ml) contains the sorbent solid (1.7 gr) being evaluated. Then, the reactor is pressurised with gas solutions until a given pressure level (120 psig). The pressure of this autoclave (reactor) during the process changes according to the chemical reaction from 120 psig to the final pressure in 24 hours approximately.

This standardised test is applied in PDVSA Intevep to measure absorption capacity at static conditions when a liquid or solid sorbent reacts with H_2S. During a given time test, the gas difference pressure (initial and final) inside the reactor reflects the amount of acid gases consumed.

$$\Delta P = P_i - P_f \Rightarrow \text{ Consumed acid gases} \tag{4}$$

In this study, the gas solution is represented only by H_2S and the solid sorbent ZnO. During this reaction, H_2S pressure (reactor pressure indeed) decreases whereas it is expected that a solid and H_2O appear as reaction product. Water does not add pressure to the system due to these thermodynamic conditions (pressure and temperature). The absorption capacity the acid gas (C_A) can be defined as the ratio of the amount of acid gas absorbed to the amount to scavenger or other sweetening agent. Equation 5 describes this relation with both quantities expressed in grams.

$$C_A = \frac{gr_{acidgas}}{gr_{scavenger}} \tag{5}$$

The gas quantity can be calculated with the ideal gas equation modified by the compressibility factor Z.

$$N = \frac{PV}{ZRT} \tag{6}$$

Where

N: number of moles
P: pressure
V: volume
Z: compressibility factor
T: absolute temperature
R: gas constant

Combining equation 4 and 5 the absorption capacity can be calculated by the following expression, considering a solid sweetening agent;

$$C_A = \frac{\frac{MV}{RT}\left(\frac{P_i}{Z_i} - \frac{P_f}{Z_f}\right)}{gr_{solid}} \tag{7}$$

Where, M is the gas molecular weight and Z_i and Z_f are the initial and final compressibility factors. As mentioned, a pressure drop implies absorption capacity of H_2S.

The grams of scavenger are the grams of the solid being studied. In the presence of water, it can be considered that the scavenger has changed by a mix of water and solid agent. In order to weight the effect of the new scavenger system (solid + water), the calculus is made with two considerations at wet conditions: in one of them the mass of scavenger considers only the solid (using the equation 7) and in the other case grams of both water and solid are taken into account according to the following equation.

$$C_{AT} = \frac{\frac{MV}{RT}\left(\frac{P_i}{Z_i} - \frac{P_f}{Z_f}\right)}{gr_{H_2O} + gr_{solid}} \tag{8}$$

Where C_{AT} is called total absorption capacity, which considers the amount of water ($gr\ H_2O$)

3.4.2. Measure Considerations

During the static absorption capacity test, the variables shown in equation 6 are:

Temperature: constant during test time (24 hours)
Pressure: It changes when the process is carried out
Volume: 50 ml, however the value V in equation 6 also considers the volume of solid agent placed inside vessel before the test and liquid water when is applied. So, the real volume is less than 50 ml. The densities of the materials allow this calculation.
$gr_{(scavenger)}$: Measured in a digital balance. In this project 1.7 gr is the test amount.
M: H_2S molecular mass is 34.1 gr/mole.
Z: H_2S is the only one gas used in this test and its compressibility factor considering the pseudo reduced parameters for its calculus.

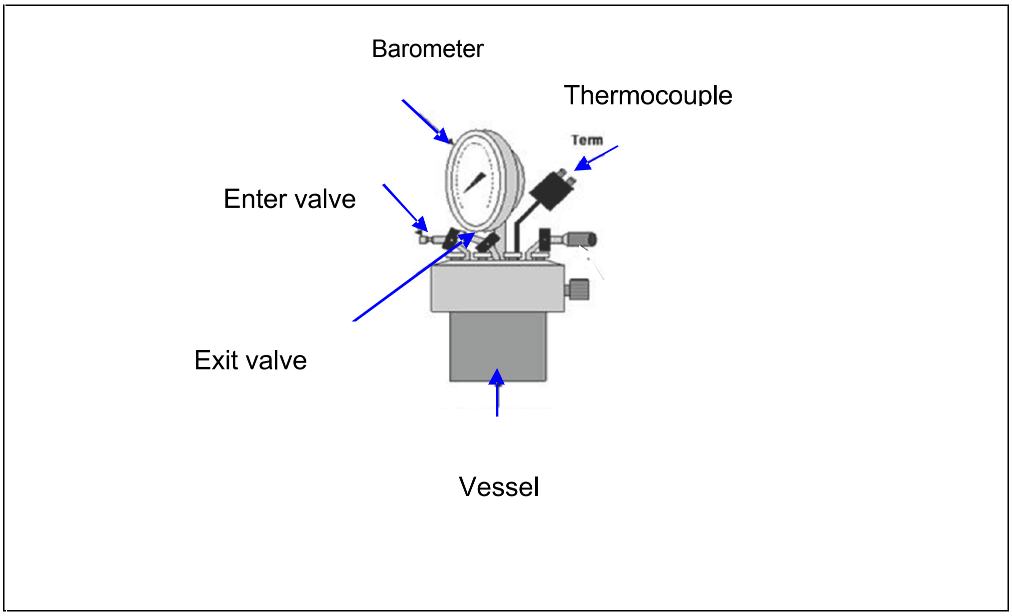

Figure 2. Part of the reactor used

3.4.3. Test conditions

The test matrix considers three main parameters that vary during absorption test. These variables are mainly focused on the two type of ZnO (nanoparticles and non nanopowder). Secondly, water absence or presence and, finally temperature. All of these conditions are illustrated in Figure 3.

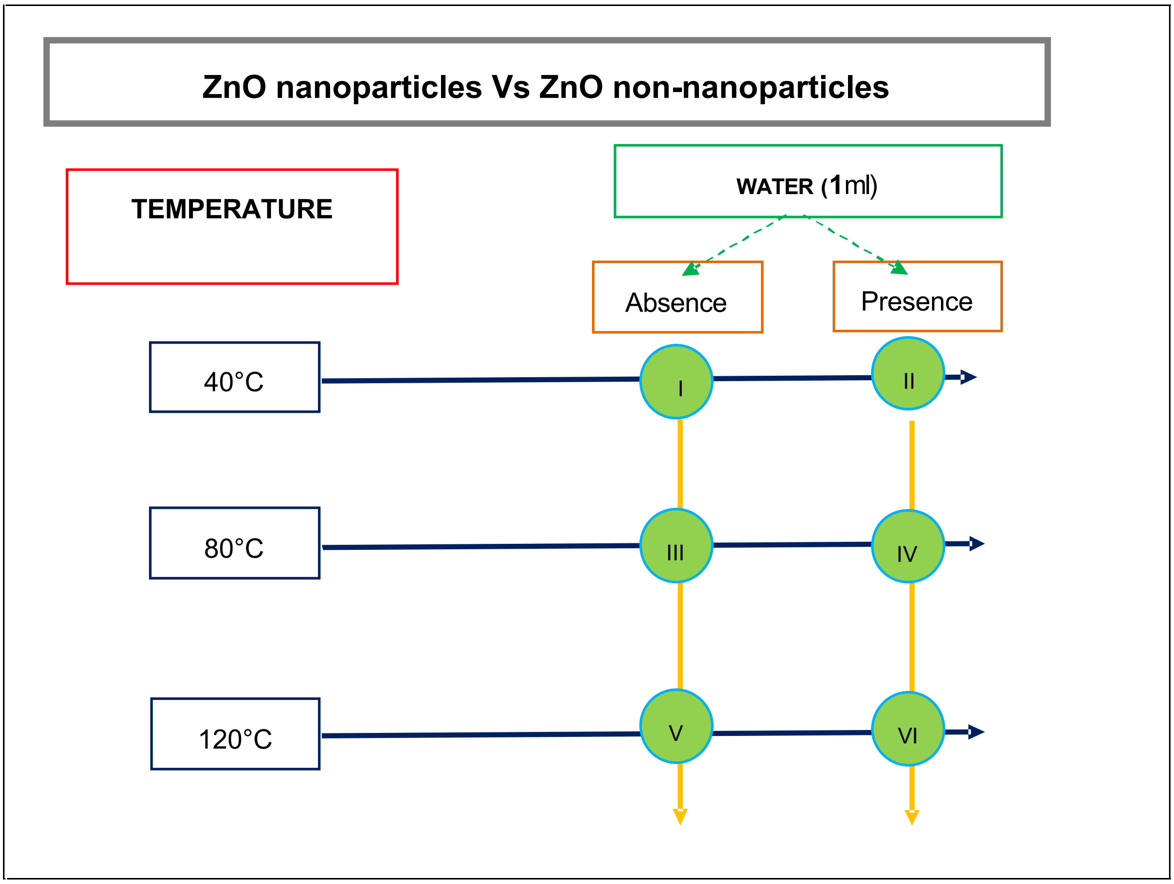

Figure 3. Matrix tests to evaluate absorption capacity of H_2S solid ZnO

Six conditions are planned (Figure 3) for each type of ZnO. The experience in each condition is repeated 4 times in order obtain an average; therefore there are a total of 58 tests. Each test requires one day or 24 hours for running.

3.4.4. Absorption capacity test procedure

The steps were:

1. The amount of solid agent (1.7 gr) was weighted using a digital balance and placed into the reactor. In case of water conditions, 1ml is also added (sprayed) on the solid agent (ZnO).
2. The lid of the autoclave was placed in position and closed. Using nitrogen as inert gas, this reactor was pressurised to check possible leakage conditions. In case of gas leak the reactor was readjusted. If not, the exit valve was opened to allow nitrogen to leave.
3. Checked non leakage, reactor was placed in the heating mantle so that it reached the programmed temperature. The heating mantle temperature was controlled.

4. When the reactor reached the temperature, then H_2S line from the cylinder was connected with the entry valve and carefully allowed this gas to flow until reaching 120 psig. After reaching this pressure, the valve was closed.
5. Time was recorded and the test was let to run for 24 hours or until the pressure was stabilised.
6. After the 24 hours, the reactor pressure was recorded.
7. The exit valve was opened to allow residual H_2S to flow into a NaOH trap and the respective reaction products were collected.

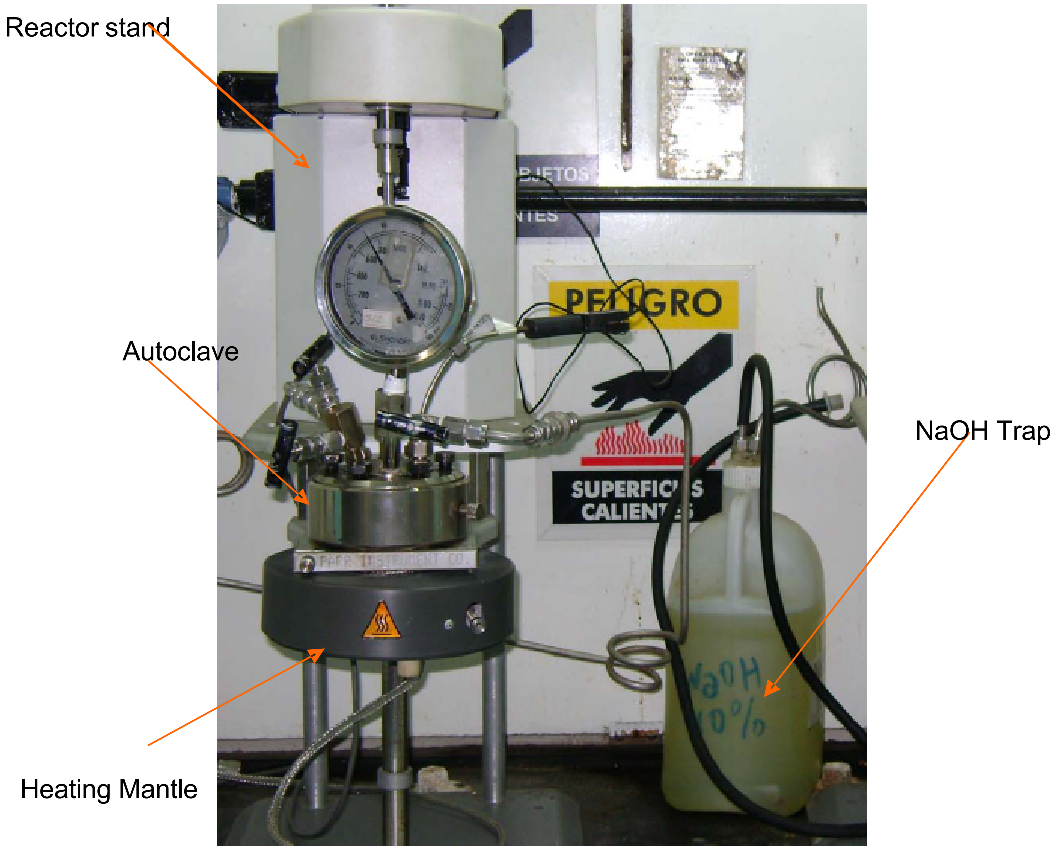

Figure 4. Absorption test system

3.5. Phases identification after the chemical reactions

The reaction products obtained in the absorption tests were labelled according to their conditions and then analysed by X-ray diffraction technique.

4. RESULTS

4.1. Physical characterisation

Results for specific surface area, pore diameter, pore volume, porosity, bulk and particle density are shown in Table 1 for nanoparticles and non nanoparticles of ZnO.

Table 1. Physical characterisation

Surface area [m^2/g]	**Pore diameter [Å]**	**Pore volume [cm^3/g]**	**Bulk density [gr/cm^3]**	**Particle density [gr/cm^3]**	**Porosity [%]**
Nanoparticles of ZnO					
41.2797	**256.05**	**0.25888**	**1.6416**	**4.5363**	**63.81**
Non Nanoparticles of ZnO					
4.9787	**120.30**	**0.014395**	**1.2703**	**1.5236**	**16.62**

The surface area of the ZnO at nanoscale demonstrates a large value in comparison with the non nanoZnO. This value is explained due to size of particles and specific surface area, in other words, smaller particles implies larger surface area.

The ZnO at nanoscale was extruded while the non nanoparticles of ZnO were not. Commonly it is expected that the surface area decreases due to an extrusion process. Since nanoparticles of ZnO were extruded by the supplier, the decrease in surface area did not avoid showing a larger surface area than any standard ZnO.

In the case of size of pore, two main parameters are presented. Regarding the difference between the surface area in two types of ZnO, the order of magnitude of the pore diameter is not so large, that the results still show that the pore size is larger at nanoscale. In case of the pore volume, the order of magnitude is totally different. In case of nanoparticles, these have almost 18 times the volume of non nanopowder per grams.

The surface area involves the external and internal area of the particles (porous area). Then, considering that pore diameters, in both cases have the same order of magnitude, the pore volume compensates so that the surface area of nanoparticles reaches this larger value.

The empty spaces of both materials of analysed ZnO are also reflected in their densities. Bulk density for nanoparticles is slightly larger than non nanopowder. In this case, the molecular arrangement of nanoparticles allows particles to take advantage of the volume. However, when it is considered the void space in a whole particle their values represented by the apparent densities are not lightly different. In this case, the pore volume plays an important role; therefore the apparent density is larger when the pore volume is also larger.

The porosity results are also connected with the values of the pore diameter and volume and densities. By this way, nanoparticles have a larger value of porosity.

4.2. Phase identification

The samples used for this analysis were divided into before and after the chemical reaction. Table 2 describes the samples. The previous stage to the chemical reaction with H_2S, refers to the samples of high purity ZnO.

Before the chemical reactions, both samples show a zincite type structure, this is another term used for hexagonal ZnO (wurtzite type).

Table 2 gives evidence that the chemical reactions occurred., after the interaction between H_2S and ZnO, It is also indicated that there are some part of ZnO that could not react with H_2S in all of the tests. The ZnO that does react with H_2S produces ZnS.

Similarly, the presence of water during the chemical reactions does not affect the crystalline structure. Only at 40°C the presence of water causes a change, in this case it could be explained by a packed change on nanoparticles before the chemical reaction.

Table 2. X-ray diffraction

Before absorption test	**Encountered phases**			
	ZnO nanoparticles		**ZnO non nanoparticles**	
	Zincite		**Zincite**	
After absorption test	**H_2O Added**	**Non $H_2$0 Added**	**H_2O Added**	**Non $H_2$0 Added**
40°C	Zincite(ZnO) Wurtzite(ZnS)	Zincite(ZnO) Spharelite(ZnS)	Zincite(ZnO) Spharelite(ZnS)	Zincite(ZnO) Spharelite(ZnS)
80°C	Zincite (ZnO) Wurtzite (ZnS)	Zincite(ZnO) Wurtzite(ZnS)	Zincite(ZnO) Spharelite(ZnS)	Zincite(ZnO) Spharelite(ZnS)
120°C	Zincite (ZnO) Wurtzite (ZnS)	Zincite(ZnO) Wurtzite(ZnS)	Zincite(ZnO) Spharelite(ZnS)	Zincite(ZnO) Spharelite(ZnS)

On the other hand, the size of particles affect the type zinc sulphide obtained. In case of nanoparticles, the crystalline structure was hexagonal before (zincite) and after (wurtzite) the chemical reaction. Both are hexagonal wurtzite type indeed, but for different compounds. In the case the oxygen atoms are replaced by the sulphur atoms without changing the type of structure.

Although, both reactions are with zincite structures for the two types of particle, in case of non nanopowder of ZnO, the type of structure is different. The replacement of oxygen atoms is accompanied by the change of type crystalline structure. Spharelite is a cubic and more dense structure and it can require less void space. It means that the tendency with non nanopowder of ZnO is not to change to any structures like wurtzite which is less dense (larger amount of volume), but spharelite or zincblende occupies less volume.

The size of the atoms of sulphur and oxygen illustrate the above explanation, and their relation with the size of unit cell for each crystalline structure. The sulphur atom is bigger than oxygen atom and their respective lattice structures follow the same tendency.

4.3. Absorption capacity test

The results indicate how effective were both types of ZnO in the scavenging process, at dry and wet conditions, and at different temperatures.

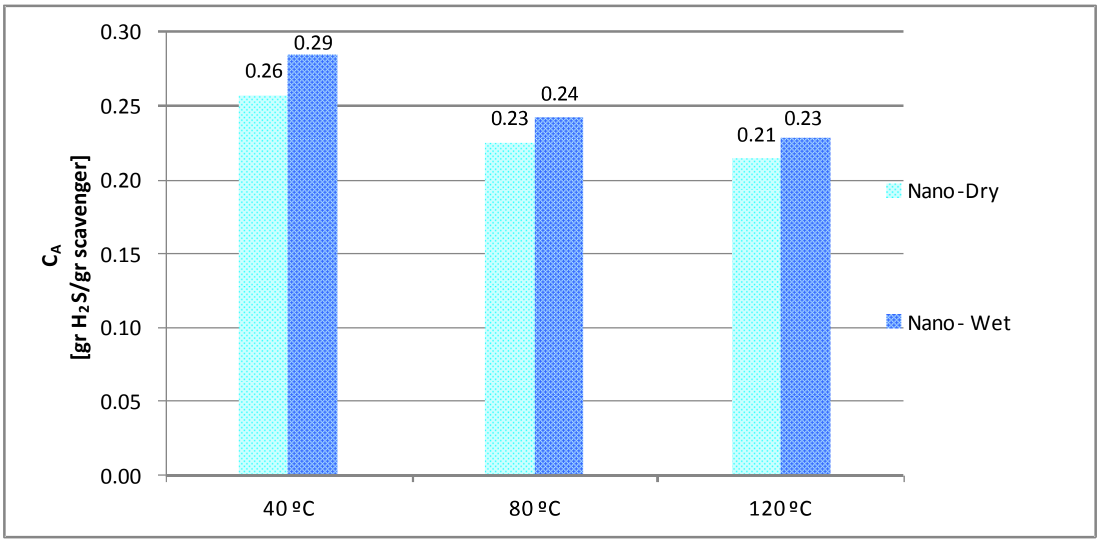

Figure 5. Absorption test of nanoparticles of ZnO

Figure 5 shows the effect of added water at three temperatures for nanoZnO. Under dry conditions, the values of absorption capacity are lower compared with wet conditions; however there is a slight difference between dry and wet condition results. The effect of water represented in Figure 5 reveals that wet condition stimulates the scavenging process. Water improves the transport process and its enhancement reaches until around 10% more than dry conditions. Likewise, in dry conditions, the effect of temperature was similar when wet conditions were used.

In the case of temperature, when this parameter increased, the absorption capacity slightly decreased. It can be explained as a diffusion process that could be activated by temperature and this mechanism competes with the large surface area that really stimulates the chemical reaction.

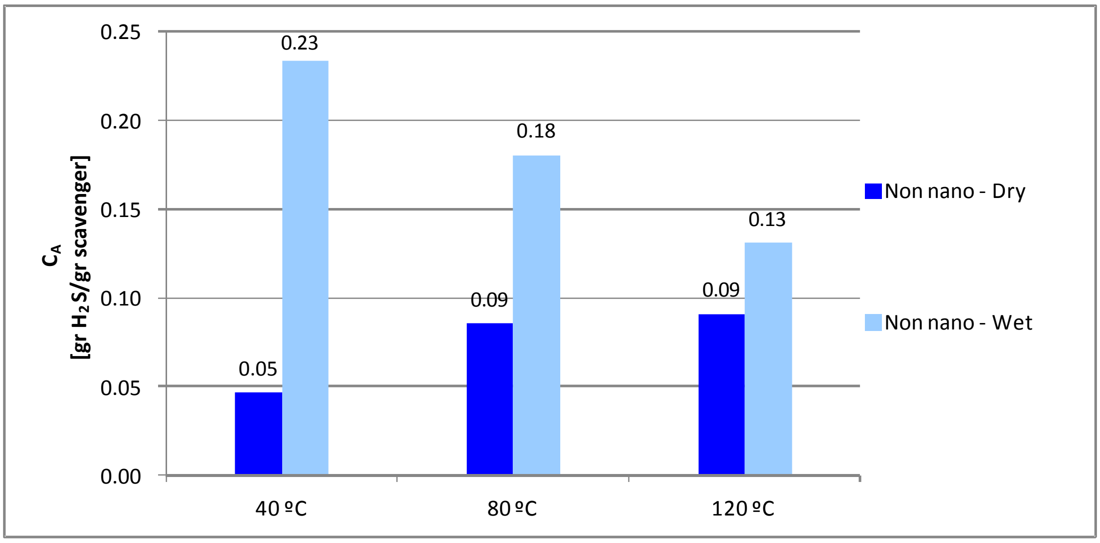

Figure 6. Absorption test of non nanoparticles of ZnO

The result for the non nanoparticles of ZnO is illustrated in Figure 6. Using dry conditions, an increase in temperature causes an increase in absorption capacity. In contrast to the case of nanoparticles of ZnO, better activation of the diffusion process by temperature had a relevant repercussion. In comparison with nanoscale, the low porosity and surface area demand high level of activation of the gas molecules of H_2S, so that these could move through and reach the ZnO surface.

In contrast with the effect of temperature at dry conditions, at wet conditions, while temperature increases the absorption capacity decreases. Furthermore, compared with dry conditions, the presence of the water caused a larger increase in absorption capacity at three temperature conditions. Consequently, this fact evidences that the water catalyses the chemical reaction. The lowest water effect on scavenging is at 120°C with a value around 43%, while the largest is around 400% at 40°C .The percentages were calculated in dry conditions.

To make a better contrast between nanoparticles and non nanopowder of ZnO, both absorption tests are shown above are joined in a single graphic (Figure 7) .

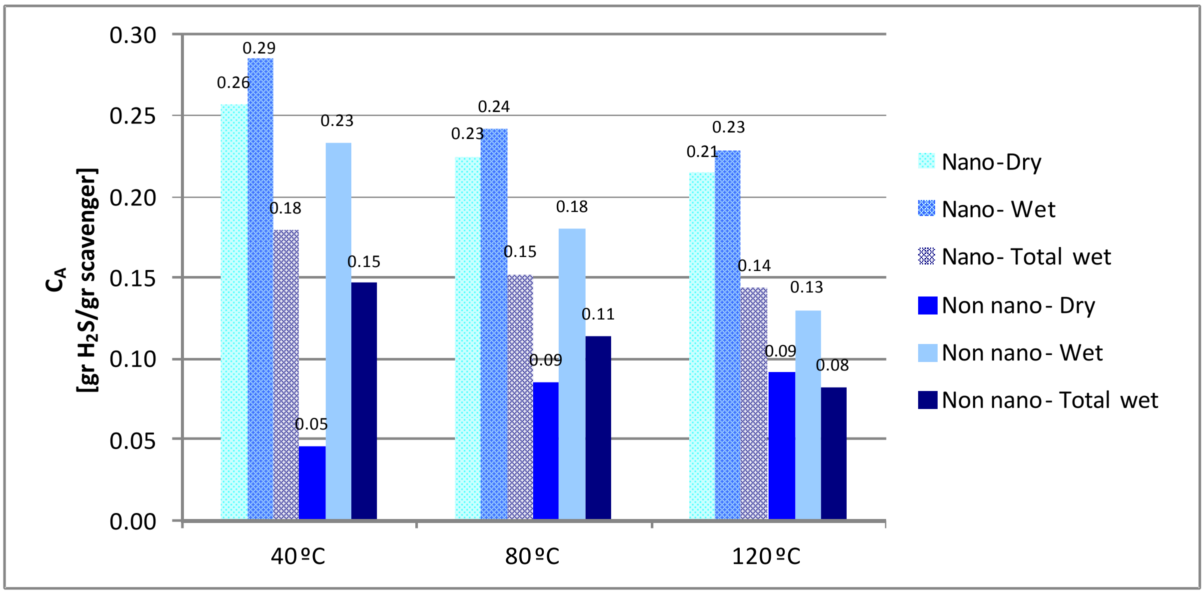

Figure 7. Overall absorption test

The high porosity and surface area of the nanoparticles of ZnO was a relevant factor which was considered to explain their better absorption capacity. At dry conditions the values of absorption capacity of nanoparticles were larger (more than twice) than the values of non nanoZnO at all temperatures conditions. Two different mechanisms are present for each type of particles: chemical reaction supported by long time contact between gas and solid in case of nanoparticles, and diffusion process helped by temperature in case of non nanoZnO.

For both type of ZnO the water enhanced the absorption capacity of H_2S, however for non nanoparticles the effect is highlighted so that it changes the tendency referred with the increase in temperature. The enhancement produced by water was larger at low temperature due to a mass transfer effect is connected with the solubility of gas in liquid. In this phenomenon the temperature has an inverse effect on solubility.

In spite of the better performance of nanoparticles of ZnO, at 40°C the enhancement by water added on the absorption of non nanopowder has the best performance almost reaching the behaviour of nanoparticles at this temperature. It means that the temperature and the water presence can be factors to be considered whether nanoscale is demanding or not.

The effect of water is very important for both systems, however the values shown in Figure 7 point out something additional; that the effect of water is better weighted through total absorption capacity (C_{AT}) that considers the amount of water added in the formula. By this way, the calculus obtained from the formula give lower than the other formula allows. However, it does not necessarily mean less H_2S consumed by the system (water + ZnO). In other words, more amounts of the mass of the system (water + ZnO) implies more amount of H_2S consumed.

5. SUMMARY

Among all the technologies employed to obtain sweet gas from sour stream, zinc oxides are commonly used in fixed solid bed and this sort of process is called scavenging. The purpose of this study is to evaluate, at laboratory scale, the performance of two sorts of ZnO as a solid agent able to take H_2S out. Due to the fact of one of these ZnO was developed at nanoscale; the main physical differences between both samples were connected with the surface area exposed to the fluid. However this work tries to find out whether or not it is required to work at nanoscale to reach acceptable behaviour of ZnO as a scavenger f H_2S, besides considering water effect.

The study showed that nanoZnO had a larger surface area and porosity, compared with the non-nanoZnO. Both samples were also analysed before and after the absorption test by X-ray diffraction and shown the evidence of chemical reactions. During the examination, both materials were evaluated by static absorption test in presence of pure H_2S during 24 hours at three different temperatures (40, 80 and 120 ºC) combined with dry or wet conditions adding a small amount of water on the samples of ZnO. At dry conditions, in case of nanoZnO, the increase in temperature caused the absorption capacity to increase, while this performance became different in case of the non-nanoZnO.

The effect of water improved the absorption capacity for both materials; nevertheless in case of non nanoZnO this effect was enhanced for two reasons. 1) These were a larger enhancement on absorption capacity in comparison with dry conditions (from 40 to 400%) besides the effect of the increase of temperature. 2) In spite of having better absorption capacity from nanoZnO at any conditions, non-nanoZnO almost reached an absorption capacity at 40 ºC similar to nanoZnO at wet conditions

6. CONCLUSIONS

- Nanoparticles of ZnO showed a higher absorption capacity than non-nanoZnO, related to the larger surface area on nanoparticles; at dry conditions. However, the enhancement on absorption capacity is not as large as the difference between the surface areas of both ZnO.
- At dry conditions, increase in temperature caused absorption capacity to increase in case of non-nanoZnO, while it was an inverse effect in the case of nanoparticles cases.
- The presence of water (wet conditions) generated an increase in absorption capacity, thus water improves the mass transfer process.
- The water effect on absorption capacity is a secondary factor on nanoparticles performance, whereas in case of non-nanoZnO it is shown that mass transfer through water has relevant repercussions on the absorption capacity, so that the mechanisms changed from diffusion at dry conditions to chemical reaction improved by water presence, at wet conditions.
- Working at nanoscale has a significant effect on scavenger process due to greater exposed surface area. Thus, between the nanoparticles and non nanoparticles of ZnO, the last ones presented lower values of: specific surface area, pore size and porosity.
- In spite of using the same phase of ZnO (Zincite) before the chemical reaction, the crystalline phases of the solid product encountered ZnS were dissimilar.